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Isolation of an Hydroxy Acid Concentrate from Wool Wax Acids[1]

THE PRESENCE of hydroxy acids in the saponifiable fraction of wool wax has been reported by a number of investigators (1, 5, 6, 7, 8, 9, 10, 13). Kuwata (8) used a combination of extraction and distillation to isolate 2-hydroxyhexadecanoic acid. Weitkamp (13) obtained the same acid and 2-hydroxytetradecanoic acid by an amplified distillation of their methyl esters. Horn and coworkers (6, 10), using a countercurrent distribution technique, obtained a 2-hydroxy acid fraction consisting of 27% of the total saponifiable fraction. The latter authors isolated 2-hydroxydodecanoic, 2-hydroxyoctadecanoic, and 2-hydroxy-16-methyl heptadecanoic as well as those acids previously reported.

Other positional isomers of the 2-hydroxy acids that have been isolated are 30-hydroxytriacontanoic acid and 32-hydroxydotriacontanoic acid (7).

In order to study the chemical and physical properties of the hydroxy and unhydroxylated acids, particularly as their heavy metal soaps, a larger quantity of acids was required than that obtained by the techniques used in earlier work. The present paper describes a method for obtaining an hydroxy acid concentrate on a large scale. Also included are additional studies on the countercurrent solvent distribution of both the wool wax acids and their methyl esters.

Preparation of Wool Wax Acids. USP lanolin was saponified according to the procedure of Barnes, Curtis, and Hatt (2), and the unsaponifiable material was removed by repeated extraction with commercial heptane. The wool wax acids were liberated by hot acidification of the sodium soap solution with sulfuric acid. The acids obtained in this manner had an appreciable ester number, presumably on account of such compounds as estolides, lactides, and lactones. The tendency for wool wax acids to esterify in this manner is so great that acid numbers decreased with increasing storage-time even at room temperature in the solid state. A corresponding increase in the ester number was also noted. The change in ester number was studied by periodically analyzing samples stored at room temperature. Over a seven-month period the ester number of one sample increased from 7.5 to 23.9. A control stored at 0°C. showed no change in ester number.

In order to reduce the ester number, the acids were resaponified with 100% excess potassium hydroxide, and the resulting soap solution was added slowly to a stirred ice-water mixture containing hydrochloric acid no more than 5% in excess over that required for neutralization of the potassium hydroxide. By using

by this procedure analyzed as follows: acid number, 160.4; saponification number, 163.6; ester number, 3.2; percentage of hydroxyl 2.48.

Fractionation of Wool Wax Acids. An attempt was made to fractionate wool wax acids between aqueous alcohol mixtures and commercial heptane (3). In one experiment 90% aqueous ethanol was used as the lower phase, in another an aqueous alcohol mixture 45% ethanol–45% methanol–10% water). In both experiments the hydroxyl content of the residual material remaining in the heptane layers was greater than the hydroxyl content of the material removed in the alcohol layers. Since the hydroxy acids were not concentrated in the more polar alcohol layers to any appreciable extent, it appeared that partition of wool wax acids between these two immiscible solvents was not a feasible fractionation scheme.

Countercurrent Distribution of Methyl Esters of Wool Wax Acids in a Craig Apparatus. Methyl esters of wool wax acids (acid number, 1; saponification number, 159.9; percentage of hydroxyl, 2.2) were partitioned in a 40-Tube Craig countercurrent distribution apparatus in order to determine partition coefficients for the hydroxy and unhydroxylated esters. Each tube of the apparatus accommodated 40 ml. of solvents (20 ml. of each layer). The solvent layers chosen were commercial heptane and the mixture of methanol-ethanol-water previously mentioned. At the completion of the distribution the entire contents of each tube was poured into a tared beaker and the solvents were evaporated. The curve shown in Figure 1

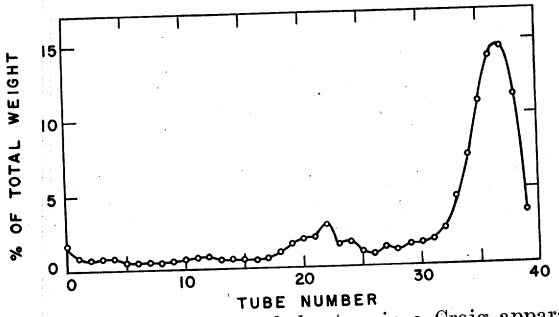

FIG. 1. Distribution of methyl esters in a Craig apparatus, using the 45% ethanol-45% methanol-10% water-heptane system.

was obtained by plotting tube number against the total amount of solute contained in each tube expressed as a percentage of the total weight of solute

efficients may be derived from the experimental curve by the following trial-and-error process. Using the application of the binomial theorem to countercurrent distribution (4, 14), an assumed value for the [illegible] solute in the tubes corresponding to the peak in question. If the calculated curve does not fit, then the process is repeated until a fit with the experimental curve is obtained. No exact values for partition coefficients could be obtained in the present instance since none of the calculated curves could be fitted to the experimental curve. However useful information could be obtained from inspection of the experimental curve. The unhydroxylated ester peak is skewed away from the hydroxy ester peak. In a separation in which the lower layer is moved (the Craig apparatus moves the upper layer), substantially all of the unhydroxylated material will remain in the apparatus while the hydroxy material is removed by a single withdrawal technique of lower layers. Increasing the concentration should skew the unhydroxylated ester peak further and help keep the bulk of this material in a few tubes or bottles (12).

Large-Scale Partitions of Methyl Esters. Thirty grams of the methyl esters were split into three equal portions. Each portion was dissolved in 100 ml. of equilibrated heptane and added to a separatory funnel. Three additional separatory funnels, each containing 100 ml. of the heptane layer, completed the extraction train. The heptane solution in each funnel, starting with the first and continuing through the extraction train in order, was extracted with 100-ml. portions of the alcohol layer (45% ethanol-45% methanol-10% water). Twenty-three extracts were withdrawn from the extraction train. The results are shown graphically in Figure 2; the last fraction withdrawn is plotted next to the last fraction remaining in the apparatus (11). The combined withdrawn fractions, having a percentage of hydroxyl of 5.07, constituted 31.3% of the charge. The combined residual fractions, having a percentage hydroxyl of 0.46, constituted 68.7% of the charge.

These results clearly indicate the superiority of methyl esters over free fatty acids in these partitions since a higher average percentage of hydroxyl is obtained for the withdrawn fractions and a lower average percentage of hydroxyl is obtained for the fractions remaining in the apparatus.

For production work a much larger quantity of methyl esters (354 g.) was fractionated by using 1-gal. Pyrex bottles and 1200-ml. portions of both layers. As in the previous case, the charge was divided into three equal portions in the first three bottles. However seven bottles rather than three completed the extraction train. Thirty extracts were withdrawn from the

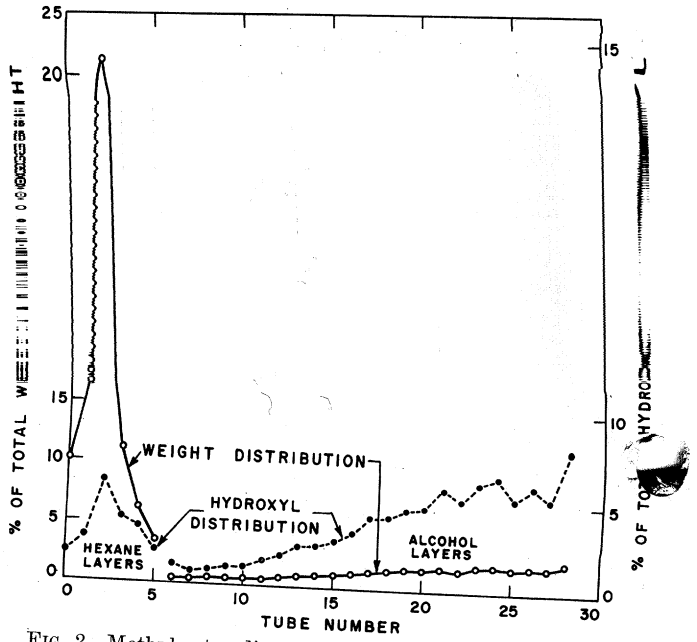

FIG. 2. Methyl ester distribution in the system 45% ethanol-45% methanol-10% water-heptane.

train. Fractions 10 to 34 of the withdrawn material, amounting to 84 g., were combined. The percentage of hydroxyl of the combined fractions was 5.5; the saponification number was 163.0; the acid number was 0.7. Fractions 35 to 38 of the withdrawn material, amounting to 18.2 g., were hard, transparent, and highly colored. They were not combined with the hydroxy esters. The residual material amounted to 240.4 g. with an hydroxyl content of 0.9%.

Summary

The fractionation of the methyl esters of wool wax acids by partitioning between two immiscible solvent layers has been described. Three fractions were obtained: a fraction rich in hydroxyl content, a fraction low in hydroxyl content, and a small amount of hard, transparent, highly colored material. The same procedure when applied to the free wool wax acids did not yield a satisfactory hydroxy acid concentrate.

The preparation of wool wax acids with an essentially zero ester number, that is, in a form free of estolides, lactides, and lactones has also been described.

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